PATENT SPECIFICATION

(11) 1 402 466

(21) Application No. 44502/72 (22) Filed 26 Sept. 1972
(31) Convention Application No. 2 148 209
(32) Filed 27 Sept. 1971 in
(33) Germany (DT)
(44) Complete Specification published 6 Aug. 1975
(51) INT CL[2] H01M 8/04//G05D 23/22, 23/24
(52) Index at acceptance
H1B F100 F304 F3X F4 F504 F506 F510 F602 F700
G3R 2A1 36BX 36F7 36H2 4 61 65

(19)

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(54) FUEL CELLS

(71) We, SIEMENS AKTIENGESELLSCHAFT, a Germany company, of Berlin and Munich, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to fuel cells.

Fuel-cell batteries consisting of a number of fuel cells are generally operated at temperatures above the ambient temperature. If the operating temperature is not reached, the full rated power cannot be extracted. However, when a fuel-cell battery is set in operation, it is desirable that the energy should be available as rapidly as possible, *i.e.* the operating temperature should be reached rapidly and preferably without any considerable expenditure of additional energy. Since the battery is not capable of operating at full output during the warm-up time, *i.e.* as long as the operating temperature has not yet been reached, it is generally attempted to shorten the warm-up time in order that energy may be extracted from the battery at the earliest possible moment.

The property of fuel cells and fuel-cell batteries which has just been described is referred to in the journal "Atom und Strom", 16th year (1970), part 5, pages 77 to 80, where there is mentioned as a property of fuel cells the fact that the thermal inertia necessitates warm-up times of about 20 minutes.

In the Conference Report II of "Journees Internationales d'Etude des Piles à combustible", Brussels, 1965, pages 16 to 21, it is stated that problems of a thermal nature arise in fuel cells and batteries. It is observed that, at the starting of a cold battery, the loss heat and the energy which under normal operating conditions would be given up externally are necessary for the warming. It is further stated therein that larger units may be provided with means for heating as well as for cooling.

For heating fuel cells and fuel-cell batteries the cell or battery may be arranged to act on a heating means in the electrolyte circuit with the excess power produced by the cell or battery and not required by an external load. In addition, the electrolyte liquid may also be heated up, inside or outside the battery, with the use of separate current. In such methods, useful output energy is available only when the operating temperature has been reached. However, it would be advantageous in many cases if the battery could supply useful output energy, even on a reduced scale, immediately after having been switched on without the warm-up time being thereby substantially lengthened.

When a fuel-cell battery is loaded below its rated capacity, the heat of reaction which is produced is generally insufficient, if it does not reach a lower threshold value, to cover the heat losses of the whole system, so that the temperature falls. On a sudden increase of load, an appreciable time may elapse before the operating temperature is reached again and the battery can be fully loaded. Endeavours are therefore made to maintain the operating temperature even on a lowering of the load in order to achieve a better degree of gas conversion and an immediate readiness for full load.

It is generally necessary to provide means whereby, when a fuel-cell battery is overloaded, a greater quantity of heat of reaction is dissipated from the battery than in normal operation, in order to prevent a maximum temperature being exceeded and accordingly thermal damage, more especially to the catalyst material and to the material of the frame of the battery being caused. It is desirable that the fuel-cell battery should be capable of operation without a reduction of output even when such a condition arises during operation.

According to one aspect of the present invention there is provided a method of operating a fuel cell, wherein electrolyte flows through the fuel cell at a rate that is

variable, an increase in the flow rate being brought about as a consequence of an increase in the temperature of the electrolyte leaving the fuel cell and a decrease in the flow rate being brought about as a consequence of a decrease in the temperature of the electrolyte leaving the fuel cell.

According to another aspect of the present invention there is provided a fuel cell, provided with a temperature sensor for sensing the temperature of electrolyte leaving the cell when it is in use, and control means connected with the temperature sensor for varying the rate of flow of electrolyte through the cell when the fuel cell is in use in such manner that an increase in the flow rate is brought about as a consequence of an increase in the said temperature and a decrease in the flow rate is brought about as a consequence of a decrease in the said temperature.

The invention may be used to provide a method of operating a fuel-cell battery with an electrolyte which flows through the battery, and is more especially circulated therethrough, which obviates the difficulties outlined above. More particularly, the invention may be used to ensure that the battery reaches its full rated output shortly after having been set in operation, and that the full rated output of the battery is obtained rapidly after it has operated below or above its full rated output.

For a better understanding of the invention, and to show how the same may be carried into effect, reference will now be made, by way of example, to the accompanying drawing, in which:

Figure 1 illustrates diagrammatically apparatus including a fuel-cell battery, and

Figure 2 shows a graph of flow rate against temperature.

Figure 1 shows an electrolyte circuit 1 having disposed therein a fuel-cell battery 2, a depletion unit 3 for water of reaction and loss heat, an electrolyte storage vessel 4 and an electrolyte pump 5. The battery 2, for example a hydrogen/oxygen fuel-cell battery, is built up of a number of fuel cells (say 50) whose electrolyte chambers are traversed in parallel by the electrolyte liquid, as indicated in Figure 1. The fuel cells may be fuel cells with supported electrodes of the kind disclosed in U.S. Patent Specifications Nos. 3,471,336, 3,480,538 and 3,554,812. The supported electrodes of the fuel cells contain, for example, pulverous Raney nickel as anode material and pulverous Raney silver as cathode material. There is employed as electrolyte liquid an aqueous solution of potassium hydroxide with a concentration substantially in the region of 6 mol/l. Hydrogen is used as combustion gas and oxygen as gaseous oxidant. The ducts for the reaction gases have been omitted from Figure 1 for the sake of clarity.

In the heat/water depletion unit 3 the water formed in the electrochemical reaction in the fuel-cell battery, which dilutes the electrolyte, and at the same time also loss heat which is formed in this reaction, and which causes heating-up of the electrolyte liquid, are removed. A suitable form of apparatus is described in Austrian Patent Specification No. 277,341.

The electrolyte circulation is effected with the pump 5, which at the same time serves as a control element for the flow of electrolyte through the battery. The pump 5 is a speed-controlled sleeve-gapped pump driven by a commutator-less direct-current motor 6. Such a pump is described in "Siemens-Zeitschrift", 44th year (1970), part 6, pages 392 to 395. It is hightly reliable and has a long useful life.

For regulating the flow of electrolyte through the fuel battery 2, a temperature sensor 7, for example, a thermistor, is disposed in the electrolyte circuit 1, directly at the outlet of the battery. Thus, a resistor having a high negative temperature coefficient of resistance is employed for determining the temperature of the electrolyte. There may alternatively be employed as the temperature sensor a thermo-couple or a resistance thermometer, for example.

The temperature sensor is preferably disposed at the point of highest temperature in the electrolyte circuit. It may be disposed within the battery at the downstream end thereof instead of outside the battery immediately adjacent the battery outlet. The electrolyte temperature determined by the temperature sensor acts as reference input on a speed control loop in which there are disposed the motor 6 and a regulating unit 8. The regulating unit 8 is connected to control the supply of operating energy to the motor from a source of 24V direct current.

The throughflow of electrolyte is controlled in such manner that, when the battery is first set in operation, the operating temperature is rapidly reached by complete or substantially complete stoppage of the electrolyte circulation, and that the operating temperature is maintained at least approximately constant during operation in the event of changing load on the battery by variation of the speed of throughflow of the electrolyte.

Thus, there is no or scarcely any circulation of the electrolyte when the battery is cold. In addition, no heating means are provided in the electrolyte circuit, so that the whole battery output can be employed as useful energy. The heat of reaction which is developed in the battery and which is greater when the battery is cold

than when it is in the operating condition, heats up only the electrodes and the battery block. Moreoever, no heat is consumed for heating up the quantity of electrolyte present outside the battery block in the ducts and the storage vessel, or for heating up ducts and heat exchangers and for dissipation of heat therefrom by conduction and radiation. As the battery temperature approaches the operating temperature, the circulation of electrolyte is slowly increased, while the component parts disposed outside the battery are slowly heated up. The increase of the circulation of electrolyte is so regulated that the battery temperature does not fall, but steadily rises to the operating temperature. In this way, maximum possible useful energy can be obtained with a short starting-up time.

If the loading of the fuel battery falls during operation, the temperature of the electrolyte decreases when a particular limit is reached, as already stated. However, the circulation of electrolyte is throttled even on a small temperature drop, so that the quantity of heat removed from the battery by the electrolyte is reduced, and the heat losses in the electrolyte circuit are lowered. Therefore, recourse to additional heating means, which is necessary in certain circumstances for maintaining the operating temperature on loading below the rated capacity, is necessary only on a further reduction of the loading and hence on a further drop of the electrolyte temperature. Therefore, the lower loading limit at which the operating temperature falls is lowered without additional expenditure of energy, so that the maintenance of the state of operation, a good utilisation of the reaction gases and complete readiness for operation can be maintained over a longer period of time than was possible hitherto.

If the fuel battery is overloaded during operation, more heat of reaction is formed, and this must be extracted from the battery by the electrolyte liquid. This is achieved by increasing the flow rate of electrolyte through the battery. In this way, heat is removed from the battery without lowering the inlet temperature of the electrolyte, i.e. the original temperature difference between the inlet and outlet temperatures of the electrolyte is maintained. Disadvantages which might arise on lowering of the temperature at which the electrolyte enters the battery are therefore avoided. Thus, the output capacity of the battery can be raised and the battery can be more highly overloaded. The aforesaid disadvantages might arise owing to the fact that, with a constant flow of electrolyte through the battery, a greater temperature difference would be necessary between the temperature at which the electrolyte enters the battery and the temperature at which it leaves the battery in order to dissipate the increased quantity of heat by means of the electrolyte liquid. However, since a maximum temperature must not be exceeded, as already explained, the electrolyte inlet temperature would then have to be lowered. This in turn would result in a cooling at least of those parts of the electrodes at the inlet to the battery, which would cause a reduction in output.

In the case of Figure 1 the throughflow of electrolyte is regulated by an electronic circuit with the aid of the regulating unit. Alternatively, the flow of electrolyte through the battery may be regulated by a throttle valve whose degree of opening is regulated (mechanically actuated) by the temperature sensor 7, in which case a constant-speed pump would be employed to circulate the electrolyte liquid.

Figure 2 illustrates a characteristic curve for the control of the throughflow of electrolyte in dependence upon the temperature sensed by the sensor 7. Values of the rate of flow in litres per hour are plotted as ordinates and the values of the electrolyte temperature in degrees C. are plotted as abscissae. Typical values represented by the characteristic curve illustrated in Figure 2 are the following:

Electrolyte temperature in °C.	25	59	60	70	75	80	81
Throughflow in litres per hour	0.6	0.6	6	35	75	240	330

The rated power of a fuel-cell battery consisting of 50 fuel cells may be 1.9 kW at an operating temperature of about 80°C. The throughflow of electrolyte at the rated power is about 240 l/h, *i.e.* 4 l/min., in accordance with the characteristic curve of Figure 2. The throughflow of electrolyte is so controlled at the starting-up of the battery that, at temperatures below about 50°C., the flow through the battery is only about 10 cc/min., *i.e.* 0.6 l/h. The lower limit for the throughflow of electrolyte, which may be well below 10 cc/min., is so adjusted in each instance that the temperature sensor employed indicates the correct electrolyte temperature even at such low throughflow values. This is advantageous particularly when the temperature sensor is not disposed at the point of the highest temperature. From a temperature of about 50°C., the throughflow is increased until it reached about 240 l/h (the value for the throughflow during the state of operation) at about 80°C., which is the operating temperature at rated load.

By using a steadily rising electrolyte throughflow, the warm-up time of a battery may be considerably reduced. While the warm-up time for the described battery with constant electrolyte circulation is about 22

minutes, it can be reduced to about 14 minutes with the aid of the steadily rising electrolyte circulation as described. The period of time before which the battery is ready for full operation is consequently reduced by more than 35%.

The flow rate of electrolyte through the battery is raised above the value for operation at the rated output when the fuel battery is overloaded. Thus, on an increase of the electrolyte temperature by about 1°C. (for example from 80°C. to 81°C.) being determined by the temperature sensor, the throughflow of electrolyte increases from 4 1/min. to about 5.5 1/min., *i.e.* 330 1/h, the heat of reaction for a useful power of 2.3 kW being dissipated at the same temperature difference between the electrolyte inlet and electrolyte outlet temperatures as in the state of operation at the rated power of 1.9 kW, namely 6°C. The heat/water depletion unit is therefore so designed, for example by the incorporation of heat exchangers, that the maximum possible loss heat can be dissipated.

When the battery is loaded below its rated capacity, and the electrolyte temperature thus falls, the characteristic curve shown in Figure 1 is followed in the opposite direction, *i.e.* the flow rate of electrolyte through the battery is reduced.

The illustrated apparatus may be modified to apply it to a fuel-cell battery in which the electrolyte is not circulated, but merely flows through the battery. This is the case, for example, when the electrolyte liquid is separately stored, is used elsewhere for another purpose or is discarded, after having flowed through the battery.

WHAT WE CLAIM IS:—

1. A method of operating a fuel cell, wherein electrolyte flows through the fuel cell at a rate that is variable, an increase in the flow rate being brought about as a consequence of an increase in the temperature of the electrolyte leaving the fuel cell and a decrease in the flow rate being brought about as a consequence of a decrease in the temperature of the electrolyte leaving the fuel cell.

2. A method as claimed in claim 1, wherein the flow rate of electrolyte is varied in such a manner in dependence on variations in the temperature of the electrolyte that if the temperature of the electrolyte is below a predetermined minimum value the said flow rate is substantially zero.

3. A method as claimed in claim 1 or 2, wherein the temperature of the electrolyte is maintained substantially constant with variations in the load connected to the fuel cell by varying the flow rate of electrolyte.

4. A method as claimed in claim 1, 2 or 3, wherein electrolyte is caused to flow through the fuel cell by a pump whose pumping rate is varied in dependence upon variations in the said temperature.

5. A method as claimed in claim 1, 2 or 3, wherein electrolyte flows through the fuel cell at a rate dependent upon the setting of a throttle valve, the said setting being varied in dependence upon variations in the said temperature.

6. A method as claimed in any preceding claim, wherein a temperature sensor is employed to provide an output signal representative of the said temperature.

7. A method as claimed in claim 6, wherein the temperature sensor is a thermistor.

8. A method as claimed in claim 6, wherein the temperature sensor is a thermocouple.

9. A method as claimed in claim 6, wherein the temperature sensor is a resistance thermometer.

10. A method as claimed in claim 6, 7, 8 or 9, wherein the temperature sensor is arranged to sense the highest temperature attained by the electrolye.

11. A method as claimed in any preceding claim, wherein the electrolyte is caused to flow in a circuit.

12. A method of operating a fuel cell, substantially as hereinbefore described with reference to the accompanying drawing.

13. A fuel cell, provided with a temperature sensor for sensing the temperature of electrolyte leaving the cell when it is in use, and control means connected with the temperature sensor for varying the rate of flow of electrolyte through the cell when the fuel cell is in use in such manner that an increase in the flow rate is brought about as a consequence of an increase in the said temperature and a decrease in the flow rate is brought about as a consequence of a decrease in the said temperature.

14. A fuel cell as claimed in Claim 13, wherein the temperature sensor is a thermistor.

15. A fuel cell as claimed in Claim 13, wherein the temperature sensor is a thermocouple.

16. A fuel cell as claimed in Claim 13, wherein the temperature sensor is a resistance thermometer.

17. A fuel cell as claimed in Claim 13, 14, 15 or 16, wherein the control means comprise a pump arranged for causing electrolyte to flow through the fuel cell, drive means connected for operating the pump, and a regulating circuit connected to the temperature sensor for controlling supply of operating energy to the drive means in dependence upon the said temperature.

18. A fuel cell as claimed in Claim 13, 14, 15 of 16, wherein the control means comprise supply means for delivering electrolyte to the fuel cell at substantially constant pressure, a variable-setting throttle valve for controlling the rate of flow through the fuel cell of such electrolyte, and a regulating circuit connected to the temperature sensor for controlling the setting of the throttle valve in dependence upon the said temperature.

19. A fuel cell, substantially as hereinbefore described with reference to, and as illustrated in, the accompanying drawing.

20. A method as claimed in Claim 1, performed on a fuel cell as claimed in any one of Claims 14 to 19.

HASELTINE, LAKE & CO.,
Chartered Patent Agents,
28 Southampton Buildings,
Chancery Lane,
London, WC2A 1AT,
Agents for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1975.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

1402466 COMPLETE SPECIFICATION

1 SHEET *This drawing is a reproduction of the Original on a reduced scale*

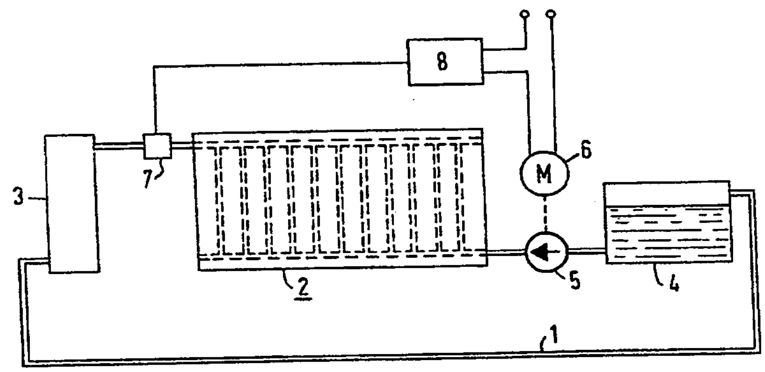

Fig. 1

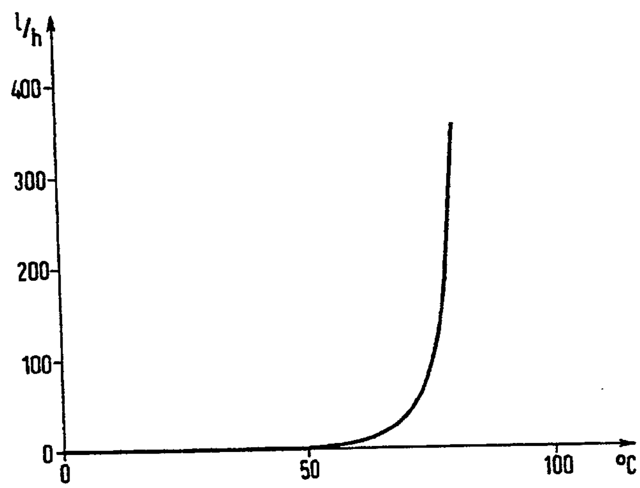

Fig. 2